Recalibration of Proton Affinities

PFI-PEPICO Yields Key Measurements with Unprecedented Accuracy

The transfer of a proton from one molecule to another is a basic chemical reaction and an important step in many biological processes. Thus, knowledge of a molecule's proton affinity—its tendency to grab hold of a proton—is highly useful in modeling or analyzing such reactions. Over 500 molecules have proton affinities whose values are known relative to each other. However, only a few key molecules lend themselves to measurements that can establish absolute proton affinity values. Such measurements have been made with unprecedented accuracy by chemical dynamics researchers using a combination of pulsed-field ionization (PFI) and photoelectron-photoion coincidence (PEPICO) techniques at Beamline 9.0.2 of the ALS. The results indicate that the current proton affinity scale should be shifted down by about 8 kJ/mol.

One of the molecules that can be used to place the proton affinity scale on an absolute footing is propene (C_3H_6). To obtain an absolute value of its proton affinity, the researchers needed to accurately measure the energy required to ionize and dissociate a precursor molecule: propyl chloride (C_3H_7Cl). This molecule can be thought of as being made up of three components: a propyl ion ($C_3H_7^+$), a chlorine atom, and an electron. The PFI-PEPICO technique used in this study can provide a very precise measure of the minimum energy required to ionize and dissociate C_3H_7Cl (i.e., its ion dissociation threshold). With an ion energy resolution of 0.5 meV, the PFI-PEPICO method improves on previous methods by almost an order of magnitude.

PFI-PEPICO takes advantage of the multibunch time structure of the ALS storage ring (512 ns of synchrotron radiation followed by a 144-ns dark gap). The ALS photons excite C_3H_7Cl molecules to energies in the vicinity of the ion dissociation threshold. While promptly produced electrons and ions are extracted by a small electric field, some neutral molecules in high-n Rydberg states remain. These need just a small energy boost to become ionized. That energy is provided by a pulsed electrical field (pulsed-field ionization, or PFI) during the 144-ns dark gap. The resultant photoelectrons provide the start signal for time-of-flight measurements of the corresponding photoions (photoelectron-photoion coincidence, or PEPICO). By measuring the relative abundance of $C_3H_7Cl^+$ vs. $C_3H_7^+$ over a range of photon energies, the researchers were able to determine very precisely at what energy the abundance of $C_3H_7Cl^+$ goes to zero (i.e., where $C_3H_7Cl^+$ dissociates completely into $C_3H_7^+$ and Cl).

This dissociation threshold energy represents the energy change that occurs when the parent molecule (C_3H_7Cl) splits into the products ($C_3H_7^+$ and Cl) or vice versa (in which case this energy is called the heat of formation). Because the heats of formation of C_3H_7Cl and Cl are well known, the heat of formation of $C_3H_7^+$ can now be determined with an accuracy limited by the error in the heat of formation of C_3H_7Cl. Then, because $C_3H_7^+$ is made up of C_3H_6 (propene) and H^+ (a proton), the heats of formation of $C_3H_7^+$ (from this work) and H^+ (well established) yield the change in energy involved in attaching a proton to propene (i.e., its proton affinity). As mentioned above, propene provides one of the absolute reference points for the scale of relative proton affinities.

Similar measurements and calculations were performed for ethylene (C_2H_4), another "anchor" molecule for the proton affinity scale. These more accurate heats of formation led to proton affinities of 742.3 kJ/mol for propene and 682.0 kJ/mol for ethylene, in good agreement with the latest theoretical calculations and about 8 kJ/mol lower than the previously accepted standard values. An example of the effect of these measurements for selected molecules having proton affinity values between 700 and 800 kJ/mole is shown. ■

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T. Baer, Y. Song, C.Y. Ng, J. Liu, W. Chen, "The Heat of Formation of 2-$C_3H_7^+$ and Proton Affinity of C_3H_6 Determined by Pulsed Field Ionization-Photoelectron Photoion Coincidence Spectroscopy," *J. Phys. Chem. A* **104**(9), 1959 (2000). T. Baer, Y. Song, J. Liu, W. Chen, C.Y. Ng, "Pulsed field ionization-photoelectron photoion coincidence spectroscopy with synchrotron radiation: The heat of formation of the $C_2H_5^+$ ion," *Faraday Discuss.* **115**, 137 (2000).

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RECALIBRATION OF PROTON AFFINITIES

PFI-PEPICO Yields Key Measurements with Unprecedented Accuracy

- **Proton affinity relevant to**
  - *Basic chemistry: acids/bases, combustion, plasmas, etc.*
  - *Biological processes: enzymes, ion transport through membranes, etc.*
- **Relative vs. absolute values**
  - *Relative proton affinities known for over 500 molecules*
  - *Absolute proton affinities established by "anchor" molecules (e.g. propene, C_3H_6)*
- **PFI-PEPICO at Beamline 9.0.2**
  - *ALS photons excite molecules to high-n Rydberg states*
  - *Time-of-flight data yield ion breakdown diagrams*
  - *Accurate ion dissociation energies measured with 0.5-meV resolution*
- **Thermochemical analysis: propene**
  - *C_3H_7Cl dissociation energy → $C_3H_7^+$ heat of formation → C_3H_6 proton affinity*
  - *New data shifts proton affinity scale down by 8 kJ/mol*

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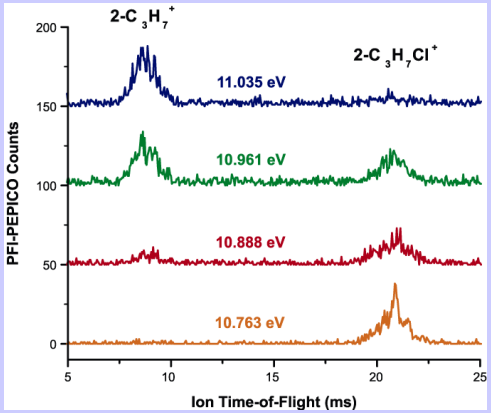
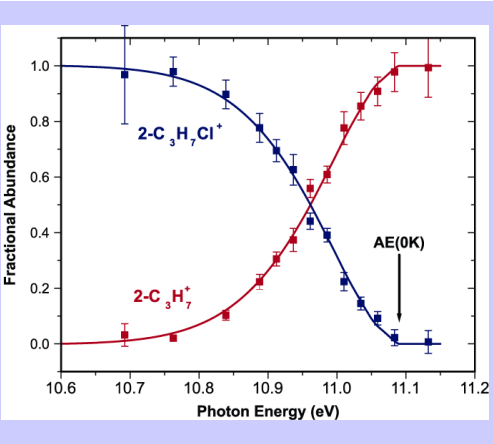
RECALIBRATION OF PROTON AFFINITIES

PFI-PEPICO Yields Key Measurements with Unprecedented Accuracy

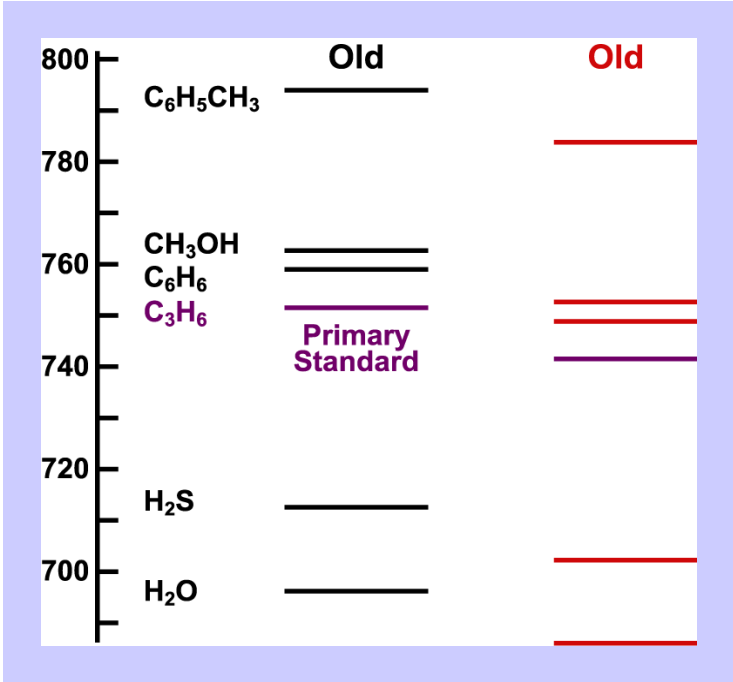


Time-of-flight distributions for $C_3H_7Cl^+$ and $C_3H_7^+$ at selected photon energies.



$C_3H_7Cl^+$ vs. $C_3H_7^+$ in the vicinity of the ion dissociation threshold, or "appearance energy" (AE) of $C_3H_7^+$ at 0 K.

Energy diagram of old and new proton affinity scales.



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